Supporting Information

Crystalline Diblock Conjugated Copolymers: Synthesis, Self-Assembly, and Microphase Separation of Poly(3-butylthiophene)-*b*-Poly(3-octylthiophene)

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Experimental

Materials. 3-Butylthiophene, 3-octylthiophene, anhydrous THF, *i*-PrMgCl in THF (2 mol/L), Ni(dppe)Cl_2, and *N*-bromosuccinimide (NBS) were purchased from Sigma-Aldrich and were used as received. 2,5-Dibromo-3-butylthiophene and 2,5-dibromo-3-octylthiophene were synthesized following the literature method.[8]

Synthesis

Poly(3-butythiophene)-*block*-Poly(3-octylthiophene). (BO50 & BO76). The molar feed ratio of 2,5-dibromo-3-butylthiophene (BT) and 2,5-dibromo-3-octylthiophene (OT) was 1:1 and 2:1 for the BO50 and BO76 samples, respectively. The molecular weight was controlled by fixing the ratio of the amount of Ni catalyst to the total monomer amount at 1:100. The typical synthesis procedure of BO50 diblock copolymer (feed molar ratio of 50:50) was as follows: two

round-bottomed flasks (250 mL) equipped with a three-neck stopcock were dried by heating under reduced pressure and cooled to room temperature. 2,5-Dibromo-3-octylthiophene (1.8 g, 5.08 mmol) was placed in one of the flasks under Ar, and then evacuated under reduced pressure to remove any water and oxygen inside. After adding dry THF (60 mL) into the flask via a syringe, the solution was mixed at 0 °C. 2 M solution of *i*-PrMgCl in THF (2.54 mL, 5.08 mmol) was added via a syringe, and the mixture was stirred at 0 °C for 30 min (solution 1). In the other flask, 5.08 mmol of 2,5-dibromo-3-butylthiophene was first reacted with *i*-PrMgCl (solution 2). Solution 1 was heated up to 35 °C and Ni(dppe)Cl_2 catalyst (53.7 mg, 0.1 mmol) was added in one portion. After stirring for 1 h, solution 2 was transferred to solution 1 via a double-tipped needle, and the resulting solution was stirred at 35 °C for overnight. The reaction was quenched by adding HCl solution (20 wt%) into the solution. The crude polymer was successively washed by Soxhlet extraction using methanol, acetone, and hexane. The solvent was removed by evaporation to give a purple solid (0.7 g, 45%). BO76 with a molar feed ratio of 2:1 (BT:OT) was also synthesized in the same manner to give a purple solid (0.6 g, 41%) as the final product. The assignment of each proton resonance in the ^{1}H NMR spectra of BO samples is as shown in Figure S1. Based on the integration of the peaks of the two resonance peaks of terminal methyl groups in butyl (e) and octyl chains (i'), the actual molar ratios of the P3BT and P3OT segments were calculated to be 50:50 and 76:24 for BO50 and BO76, respectively. The composition ratio (n:m) of BOs is calculated by the ratio of the integrated peak area of e to the integrated peak area of i' (Figure S1); [n/m= (integration of e)/(integration of i')].

BO50: ^{1}H NMR ($CDCl_3$), δ (ppm): 7.00 (1H), 2.84-2.59 (2H), 1.74-1.70 (2H), 1.52-1.34 (6H), 1.00 (1.5H), 0.89 (1.5H).

BO76: ^{1}H NMR ($CDCl_3$), δ (ppm): 7.00 (1H), 2.86-2.60 (2H), 1.77-1.67 (2H), 1.52-1.44 (3.92H),

1.02 (2.28H), 0.88 (0.72H).

Solution-Phase Self-Assembly of BO50 and BO76 and Sample Preparation for XRD, TEM, and AFM imaging. BO50 (10 mg) was dissolved in 1 mL of nitrogen degassed 1,2-dichlorobenzene (ODCB, Aldrich, anhydrous, 99%) and magnetically stirred overnight at room temperature. The resulting solution was passed through a 0.45 μm filter and allowed to stand for 24 h. In the case of BO76, the same procedure was repeated except that a 6 mg/mL solution in ODCB was prepared and a 1.0 μm filter was used. The nanowire dispersion in ODCB was drop-cast onto glass substrates and dried in a vacuum oven before XRD analysis. For TEM imaging, the nanowire dispersion was diluted 10 times with ODCB, drop-cast onto a TEM grid (300 mesh, carbon coated, copper grid, Ted Pella, Inc.) and dried in a vacuum oven. For tapping mode-AFM imaging, the dispersion was spin-coated onto a clean silicon wafer at 3000 rpm and dried in a vacuum oven.

Sample Preparation for WAXS and SAXS. Thin films of BO50 and BO76 were first casted from chloroform solutions. The thin films were annealed at 280^{o}C under high vacuum for 12h, and then slowly cooled to room temperature, allowing recrystallization from the melt state.

Characterization. ^{1}H-NMR spectra were recorded on a Bruker-AF300 spectrometer at 300 MHz. UV-vis absorption spectra were recorded on a Perkin-Elmer model Lambda 900 UV/vis/near-IR spectrophotometer. Spin-coated polymer thin films were prepared from 2 wt% solutions in chloroform. The photoluminescence (PL) emission spectra were obtained with a Photon Technology International (PTI) Inc. model QM-2001-4 spectrofluorimeter. The molecular weights reported for the polymers were determined on Polymer Lab Gel Permeation Chromatography (GPC) Model 120 (DRI, PL-BV400HT Viscometer) against polystyrene standards in trichlorobenzene at 120 °C. X-ray diffraction (XRD) patterns were measured using a

D8 Focus. The X-ray beam was nickel-filtered Cu Kα radiation from a sealed tube with a horizontal line focus operated at 40 kV and 40 mA. Data were obtained from 2-theta angles of 2^o to 30^o at a scan rate of 0.01^o/s.

AFM and TEM Imaging. TEM images were acquired on a Phillips EM420 microscope operating at 100 kV with an objective aperture to enhance the contract. TEM imaging was performed on an FEI Tecnai G^2 F20 TEM at 200 kV with objective aperture to enhance the contrast. TEM images were acquired with a CCD camera and recorded with Gatan DigitalMicrograph software. Atomic force microscopy (AFM) imaging was done with a Dimension 3100 Scanning Probe Microscope (Veeco Instruments, Inc., Woodbury, NY) operating in tapping mode. The films for atomic force microscopy imaging of surface morphology were spin-coated on a silicon wafer substrate.

Small- and Wide-Angle X-ray Scattering. Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements were performed at an Anton-Paar SAXSess instrument. The fixed sample-to-detector distance (265 mm) and wavelength (λ=0.1542 nm) provide a comparably limited q-range of 0.2~10 nm^{-1}. Here q is the scattering vector defined as $q=4\pi sin(\theta)/\lambda$, with 2θ the scattering angle. The scattering signal was collected by highly sensitive imaging plates and treated by the SAXSquant software from Anton-Paar.

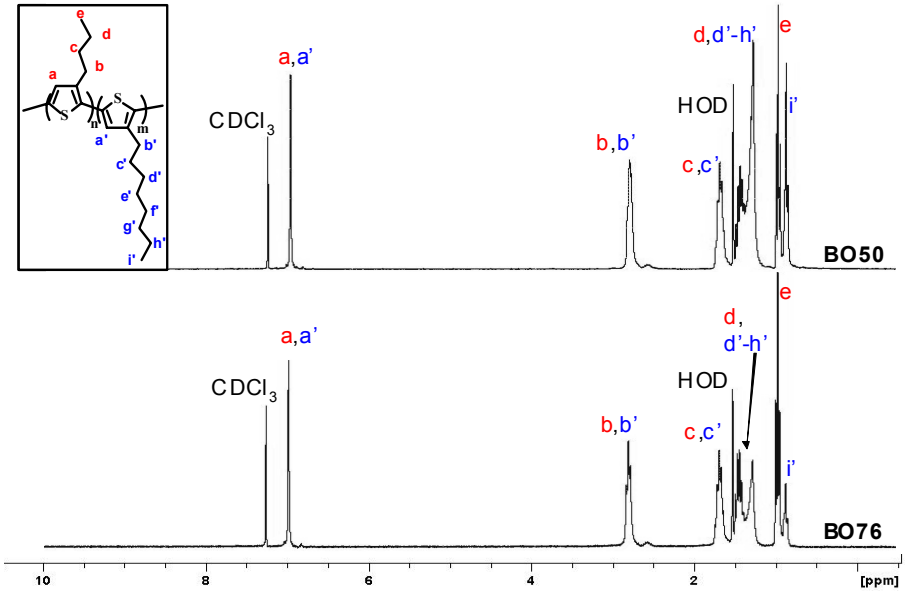

Figure S1. ^{1}H NMR spectra of BO50 and BO76 and the assignment of each proton resonance.

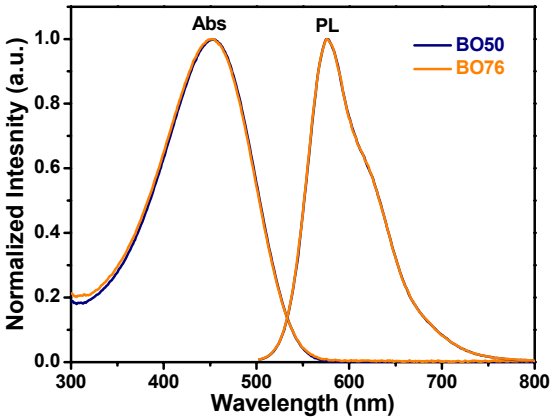

Figure S2. UV-Visible absorption and photoluminescence spectra of BO50 and BO76 in dilute chloroform solutions.

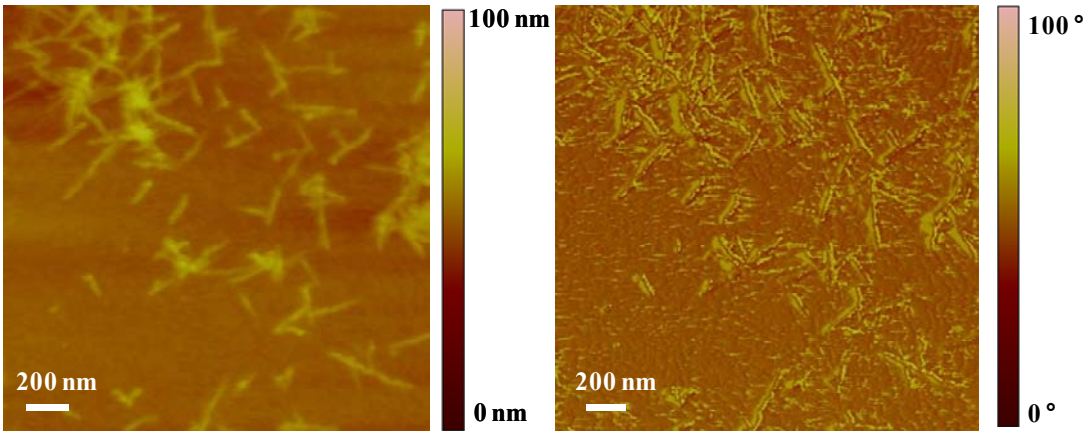

Figure S3. Tapping mode AFM topography (left) and phase (right) images of BO76 nanowires spin-coated onto a silicon wafer substrate.

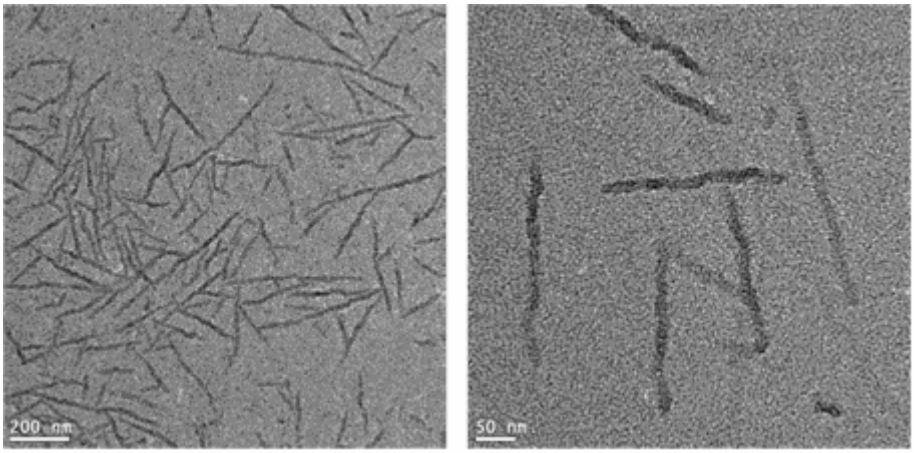

Figure S4. TEM images of BO76 nanowires at two magnifications.

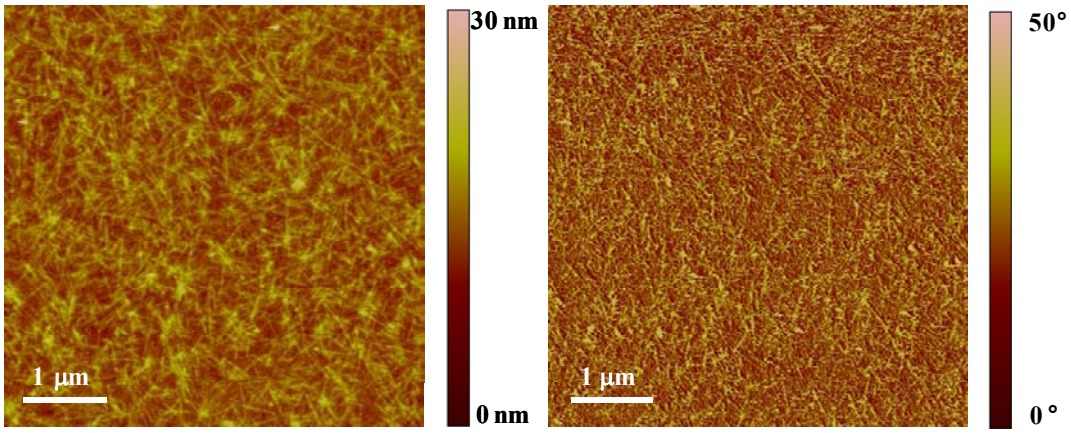

Figure S5. Tapping mode AFM topography (left) and phase (right) images of BO50 nanowires spin-coated onto a silicon wafer substrate.

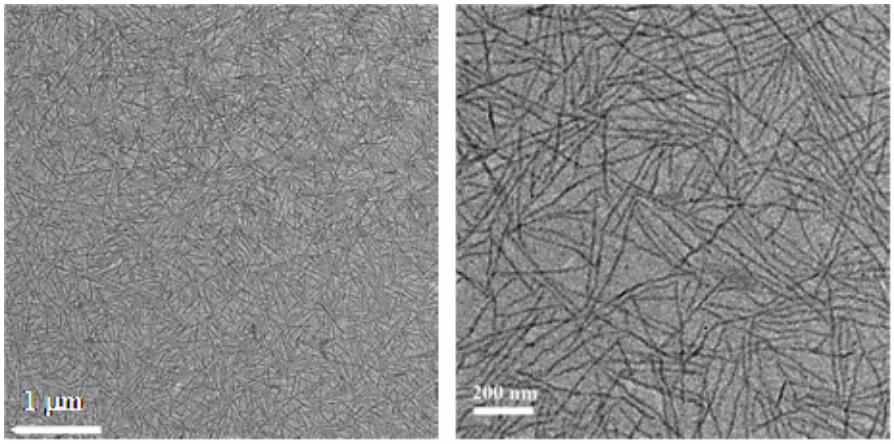

Figure S6. TEM images of BO50 nanowires at two magnifications.